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TECHNICAL REPORT*: "Studies in Hydrogen Fluoride"

A Technical Report comprising a thesis submitted by Albert William Jache to the University of Washington in partial fulfillment of the requirements for a Ph. D. degree. Work done under a contract with the Office of Naval Research.

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STUDIES IN HYDROGEN FLUORIDE

by

ALBERT WILLIAM JACHE

A thesis submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

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The author wishes to express his appreciation to Dr. Cady for his advice, encouragement, and assistance. Thanks are also extended to the fluorine group as a whole as well as to other members of the Chemistry Department for advice offered and for the pleasant atmosphere which was maintained in the laboratory.

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STUDIES IN HYDROGEN FLUORIDE

INTRODUCTION

Hydrogen fluoride is a compound with physical properties (Table 1) remarkably like those of water. The following investigations were carried out to see whether chemical behavior analogous to that of water could be detected.

This work was done in four phases. At first exploratory work was done to observe, if possible, amphoteric behavior of certain fluorides of metals. This work led to attempts to detect the formation of compounds analogous to the hydrates of substances such as the rare gases, the hydrocarbons or the halogens. An attempt was then made to develop cells involving metal, metal fluoride electrodes. It was anticipated that measurement of the potentials and temperature coefficients of electromotive force would yield useful thermodynamic data. Finally, the solubilities of twenty-nine metal fluorides were measured over a limited temperature range.

Simons (1) and Jander (2) have reviewed most of the work done in solutions of hydrogen fluoride. They have shown that it is a good ionizing solvent and that it has a tendency to form addition compounds with other substances.

Since hydrogen fluoride has a high polarity with a small atom on the negative end of the dipole it is not surprising that it combines with

TABLE 1

PHYSICAL PROPERTIES OF HYDROGEN FLUORIDE

1. Change of State

Boiling Point	19.5°C (11)
Melting Point	-83°C (12)
Critical Temperature	230.2°C (13)
Heat of Fusion	1094 cal. per 20.01 grams (12)
Heat of Vaporization (experimental)	97.5 cal. per gram (14)
Vapor Pressure	$\log P_{mm} = 7.3739 - \frac{1316.79}{T}$ (15)

2. Thermodynamic Properties

Functions based on $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) = HF\ (g)$

$\Delta H^\circ_{298.1} = -64100$ cal. per 20.01 g. HF (16)

$\Delta F^\circ_{298.1} = -64910$ cal. per 20.01 g. HF (16)

Other Thermodynamic Properties

Specific Heat (liquid) $15.51 - 5.38(10)^{-2}T + 2.18(10)^{-4}T^2$ (12)
cal. per 20.01 g. for range 200° - 270° K (17)

3. Other Properties

Specific Conductivity $1.4(10)^{-5}$ ohm^{-1} cm^{-1} (18)

Surface Tension $= 40.7 \left(1 - \frac{T}{503.2}\right)^{1.78}$ dynes per cm (19)

Viscosity $\log \eta = -4.282 - 6.372(10)^{-3}T + \frac{806.1}{T}$ (η is in millipoise) (20)

Dielectric Constant (0°C) 83.5 (21)

Liquid Density $= 1.0020 - 2.2625(10)^{-3}t + 3.125(10)^{-6}t^2$ g. per cc (19)

(range - 75°C to 4°)

fluoride ion forming numerous acid fluorides. Systems involving hydrogen fluoride and water (3), ammonia (4), potassium fluoride (5), rubidium fluoride (6), cesium fluoride (7), antimony pentafluoride (8), or silicon tetrachloride (9) have disclosed a large number of such compounds. In addition several weak organic bases as well as other inorganic compounds form hydrofluorides.

The long chain-like structure (10) of solid hydrogen fluoride might be expected to lead to clathrate compounds such as crystalline compounds with the rare gases, hydrocarbons, or halogens.

Very few attempts to measure cell potentials in hydrogen fluoride have been described. Simons and Hildebrand (22) reported that they found fluorine electrodes to be irreversible. Large overvoltages have been observed when producing fluorine from potassium fluoride-hydrogen fluoride melts by electrolysis. The potential of the normal fluorine electrode has been calculated to be 2.85 ±0.05 volts (23). The potential of the cell H_2 / HF(HF) / F_2 has been reported as 2.708 volts at 0°C (24).

The data available on solubilities of inorganic compounds are largely qualitative. They have been tabulated by Simons who lists the following fluorides as soluble (probably over 1%): ammonium fluoride, lithium fluoride, sodium fluoride, potassium fluoride, rubidium fluoride, cesium fluoride, argentous fluoride, and thallous fluoride. Beryllium fluoride, magnesium fluoride, calcium fluoride, strontium fluoride, and barium fluoride are listed as slightly soluble. The insoluble fluorides are given as zinc fluoride, cadmium fluoride, mercuric fluoride, ferric fluoride, ferrous fluoride, nickel fluoride, cobalt difluoride, aluminum difluoride, lanthanum fluoride, bismuth trifluoride, lead difluoride,

tin tetrafluoride, chromium trifluoride, cerium trifluoride, manganese difluoride, arsenic trifluoride, silicon tetrafluoride, carbon tetrafluoride, and antimony pentafluoride. Bond and Stowe (25) found chromium fluoride to be soluble. The phase system antimony pentafluoride-hydrogen fluoride (8) indicates considerable solubility. Lithium fluoride has been reported to be soluble to the extent of 0.0206 moles (27) at 18°C, and 0.045 moles (25) at 20°C per mole (20.01 grams) of hydrogen fluoride. Potassium fluoride gives a saturated solution containing 0.89 (5) mole fraction while an earlier report gives 0.84 (27) mole fraction HF at 0°C. The solubility of silver fluoride (27) has been given as 33 grams for 100 grams of solution at -15°C.

I. AMPHOTERIC BEHAVIOR

Experimental

The following exploratory survey was made to learn whether certain fluorides are amphoteric in liquid hydrogen fluoride, just as some hydroxides are in water.

Experiments were carried out using commercial liquid hydrogen fluoride contained in an aluminum phosphate glass beaker open to the atmosphere but surrounded with dry ice which furnished a protective dry blanketing layer of carbon dioxide and kept the vessel close to dry ice temperature. The aluminum phosphate glass was attacked only slightly by the liquid. Its use permitted one to observe visually the effects of adding different reagents.

Results

Zinc fluoride was found to be suostantially insoluble in hydrogen fluoride and the addition of sodium fluoride did not appear to increase the solubility as would be expected from the analogy with zinc hydroxide and sodium hydroxide in water. Addition of ammonium chloride also gave no observable effect, indicating that a complex ammonia ion was not formed.

Cupric fluoride did not appear to be soluble in hydrogen fluoride either by itself or in the presence of sodium fluoride or ammonium chloride.

Conclusions

No visually observable effects occurred in these studies to indicate amphoteric characteristics or tendency to form ammine complexes by zinc or copper.

II. HYDROGEN FLUORIDE ADDITION COMPOUNDS

Experimental

The object of this investigation was to do some exploratory work to see if hydrogen fluoride would easily form solid compounds with non-ionic, relatively inert compounds. One might expect the formation of compounds analogous to the hydrates of the rare gases, hydrocarbons, or chlorine and bromine.

This work was done with hydrogen fluoride distilled directly from a cylinder of commercial hydrogen fluoride into an aluminum phosphate glass beaker surrounded by dry ice which kept the beaker close to dry ice temperature. The rising carbon dioxide gas kept atmospheric moisture away. Small amounts of the solute were added to the solvent, with shaking or with stirring by a copper wire. The presence of solid was anticipated as evidence of compound formation.

Ethyl chloride was tried first. It was somewhat soluble but gave no evidence of solid formation.

Normal pentane did not give any evidence of solubility or of solid formation.

When methylene chloride was added to hydrogen fluoride it appeared to be somewhat soluble, but two layers appeared on standing. The layer of smaller volume was dark and the layer of larger volume had a white turbid appearance. On passing the white layer through a sintered aluminum phosphate glass plug the color cleared, perhaps be-

cause it warmed enough to increase the solubility. No solid was filtered out.

Chlorine was bubbled through liquid hydrogen fluoride giving a yellow bottom layer which was probably liquid chlorine. The upper layer was a pale yellow solution of chlorine in hydrogen fluoride. There seemed to be a thin layer between these two which appeared to contain some fine white particles. When pieces of dry ice were added, a yellow solid appeared at the bottom. This might have been a chlorine-hydrogen fluoride addition product, a chlorine-carbon dioxide addition product, or, probably, dry ice colored by chlorine. When more chlorine was added to the solution only the yellow liquid layer and the pale yellow top layer remained.

Conclusions

Ethyl chloride and normal pentane do not seem to form solid hydrogen fluoride addition compounds under the conditions described.

Methylene chloride and liquid chlorine might form solid hydrogen fluoride addition compounds under the conditions described. To definitely settle the question further work is necessary on these compounds as well as on others.

Since this did not appear to be a very hopeful field to study, it was decided to explore further to find a more promising project.

III. CELL POTENTIALS

Experimental

The object of this work was to measure the potentials of some cells made up of metal-metal fluoride electrodes or gas electrodes, and to calculate thermodynamic data from these potentials.

The hydrogen fluoride used in these cells was carefully purified by a method similar to that of Simons (26). A melt approximating KF•3HF was made up from KF•HF (Harshaw) and anhydrous hydrogen fluoride (Harshaw) in a steel cylinder. Water and other impurities were decomposed by electrolysis using the cylinder as the cathode and a nickel rod as the anode. Electrolysis was carried on at about five amperes for at least two hours after fluorine was first produced at the anode. This procedure should have oxidized any anions other than fluoride ion. This cylinder was then connected to a copper distilling column, and hydrogen fluoride was distilled off and collected as a liquid in a polythene vessel. The acid was later distilled through polythene tubing to the container where it was used. (Data on the resistance of polythene to hydrogen fluoride appears in a later section of this report.) The system was vented to the atmosphere through a liquid air trap connected to a drying tube. Connections in the polythene equipment were made through Teflon adapters or by welding. Samples of hydrogen fluoride prepared in this manner showed a specific conductance of 7.6×10^{-4} ohm^{-1} cm^{-1}.

Most of this work was done in an H-cell constructed of Kel-F

(polytrifluoromonochloroethylene). This cell had a stopcock in the cross piece which was kept closed except during measurements. The plug of this stopcock was of Teflon and required no lubrication. The cell also had platinum leads sealed into the bottom so that contact could be made with amalgams within. In addition, tubing led down into the legs to serve as gas carrying tubes when gas electrodes were used. Platinum wires which were sealed into these tubes acted as contacts for gas electrodes or as connections to solid metal electrodes. The connection was made by melting the metal in a glass tube and inserting the platinum wire. After cooling, the glass was broken and the electrode was cleaned.

Another H-cell was constructed of two eight ounce polythene bottles connected by a short piece of half inch polythene tubing. One of these bottles had three necks and the other was built to hold two gas electrodes. This made a convenient way of changing electrodes and of having more than one electrode of the same kind in the same arm. The electrodes were metals bonded to platinum wires which were sealed through the screw caps of the bottle.

A few exploratory experiments were done in open pots and in single polythene bottles which had several electrodes sealed into the side of the bottle. An H-cell made of three pieces of half inch polythene tubing was also used.

The hydrogen fluoride used was saturated with lithium fluoride to increase conductivity and to give a definite activity of fluoride ion. The lithium fluoride was put in the cell before the solvent was added. A coating of fluoride on the metal electrode was formed by electrolysis, using the metal electrode as the anode.

Most of this work was done in an air thermostat the temperature

of which was controlled within ±0.2 C as measured with a copper-constantan thermocouple at 0°C.

Results

Several cells were made up in the Kel-F H-tube with saturated zinc and lead amalgam electrodes. All of these cells were irreversible. The values read on the potentiometer depended upon the direction from which balance was approached. If the balance point was approached slowly, it was possible to "chase" the value higher and higher if it was approached from the low side, and lower and lower if approached from the high side. This was typical of most of the other electrodes too. The values obtained by a rapid approach to the balance point were not reproducible. Additional electrolysis to give more of the metal fluorides did not seem to improve the situation. The potentials most often encountered ranged between 0.2 and 0.5 volt with zinc negative. In some cases potentials as high as 1.5 volts were recorded and a few potentials of the opposite sign occurred.

A cell using pure iron and lead electrodes was assembled. These electrodes were coated with their metal fluorides in the usual manner. Their behavior was again irreversible, giving potentials usually between 0.3 and 0.4 volt with lead negative. The lead electrode was almost consumed, presumably by conversion to the fluoride during electrolysis.

Zinc and cadmium metal electrodes coated with fluoride gave irreversible cells. However the potentials recorded were more nearly consistent than most. They ranged from 0.33 to 0.36 volt, cadmium being negative.

Electrodes consisting of a piece of copper sheet, a stick of

cadmium, a stick of zinc, a piece of sheet lead, and a platinum wire were sealed into a polythene bottle which was then filled with electrolyte solution. After all the electrodes except platinum were given their electrolysis treatment, potentials were read between all possible combinations of electrodes. Potentials were calculated for third electrode pairs from two measured electrode pair potentials. They did not agree with the measured potentials in any case. This work was repeated with the same sort of results. The ranges of the potentials measured for each couple are given below. The first electrode mentioned is the negative one.

Cd-Pb	0.03 to 0.07 volts
Cd-Zn	-0.09 to 0.23
Cd-Cu	0.60 to 0.84
Cd-Fe	0.22 to 0.67
Zn-Fe	0.01 to 0.28
Zn-Cu	0.54 to 0.67
Pb-Zn	-0.1 to 0.6
Pb-Fe	0.01 to 0.4
Pb-Cu	0.58 to 0.72
Cu-Fe	0.23 to 0.34

It seemed from this work that some of the combinations involving the copper electrode were better behaved than most of the others. A cell was made up using fluoride coated copper and zinc metal electrodes. A bare platinum wire in the electrolyte was also incorporated in the cell. Potentials were read across the copper-zinc couple, across the zinc-platinum wire couple, and across the copper-platinum wire couple. Addi-

tion of the potentials measured with the platinum did not give the same value as the potential measured across the copper-zinc couple. The potentials across the latter ranged from 0.4 to 0.6 volt, with zinc negative. At the time that the copper-zinc couple gave values of about 0.45 volt, the copper-platinum wire couple gave 0.28 volt and the zinc-platinum wire couple 0.80 volt. The zinc and copper electrodes were negative relative to the platinum wire.

When a cell was made up of fluorine and hydrogen electrodes using platinized platinum, the potentials recorded ranged from 0.14 to 0.45 volt. The flucrine was diluted with nitrogen about twenty to one. When two apparently identical hydrogen electrodes were connected by a T-tube to the same source of hydrogen, potentials between the two as high as 0.3 volt were recorded. The potential seemed to be a function of the differences in bubble rates through the electrode tubes. With good bubble rate adjustment the potential was reduced to as little as a few thousandths of a volt. When these same electrodes were placed in water the potential between them dropped to zero and was not affected by flow rates.

When an H-cell was used with three fluoride coated zinc electrodes in one arm, potentials between the various pairs were as high as 0.1 volt. Potentials recorded using one of the zinc, zinc fluoride electrodes and one of the two hydrogen electrodes in the other arm as a cell combination did not check with values obtained by using the other possible combinations. The potentials recorded ranged from 0.24 to 0.48 volt, zinc being positive.

Voltage-current curves (Plate I) taken across the two platinum electrodes (the two hydrogen electrodes with no hydrogen flowing), two

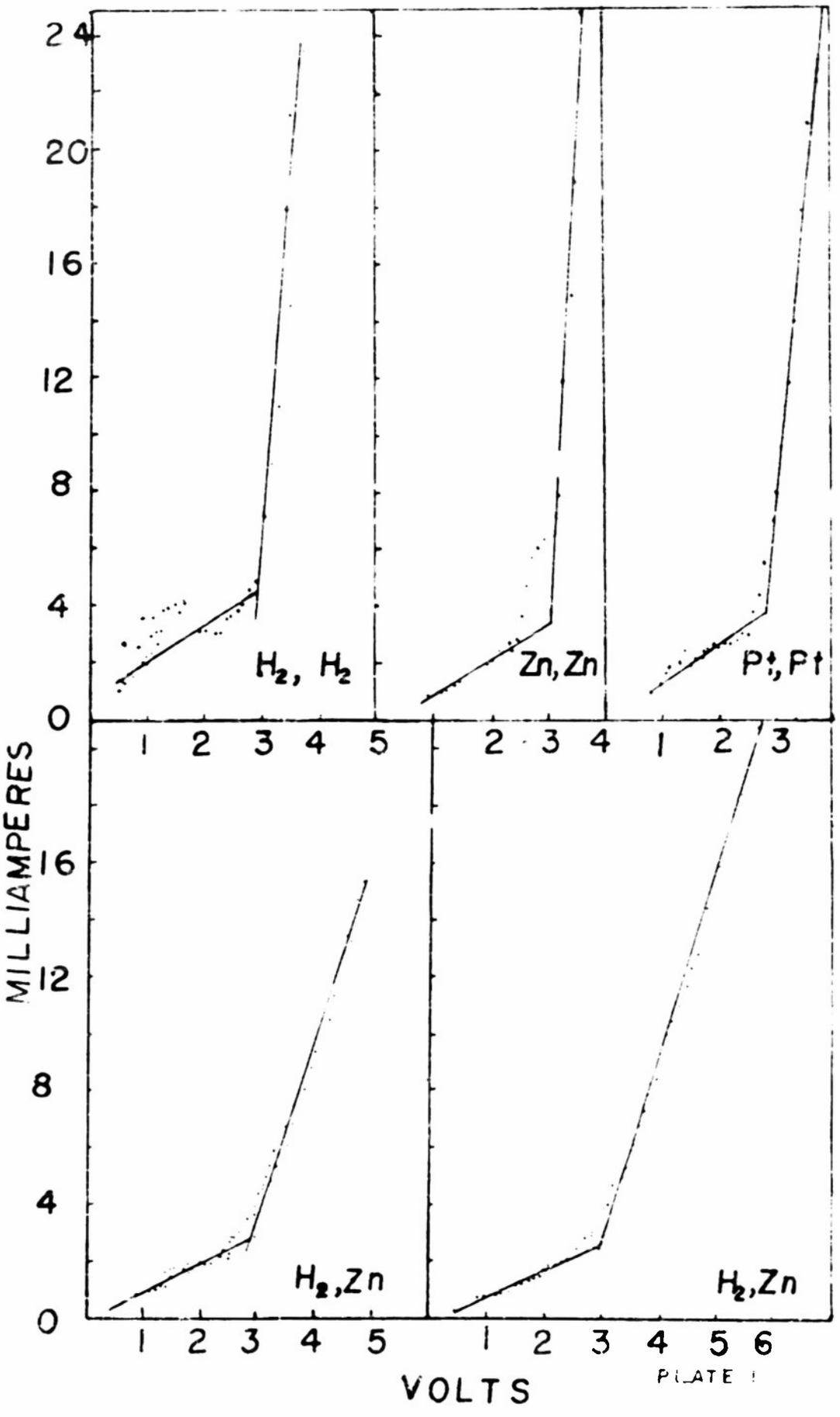

24
20
16
12
8
4
0
H_2, H_2
Zn, Zn
Pt, Pt
1 2 3 4 5
2 3 4
1 2 3
MILLIAMPERES
16
12
8
4
0
H_2, Zn
H_2, Zn
1 2 3 4 5
1 2 3 4 5 6
VOLTS

PLATE I

hydrogen electrodes, two zinc, zinc fluoride electrodes, and two different pairs of hydrogen and zinc, zinc fluoride electrodes all showed breaks at about 2.9 volts. These were recorded with a voltmeter reading directly to five hundredths of a volt and a milliammeter reading to two tenths of a milliampere. This seems to indicate a high overvoltage associated with all of the electrodes.

Discussion and Summary

None of the electrodes tried gave reversible or reproducible potentials. With reluctance it was decided that work on this subject should be dropped.

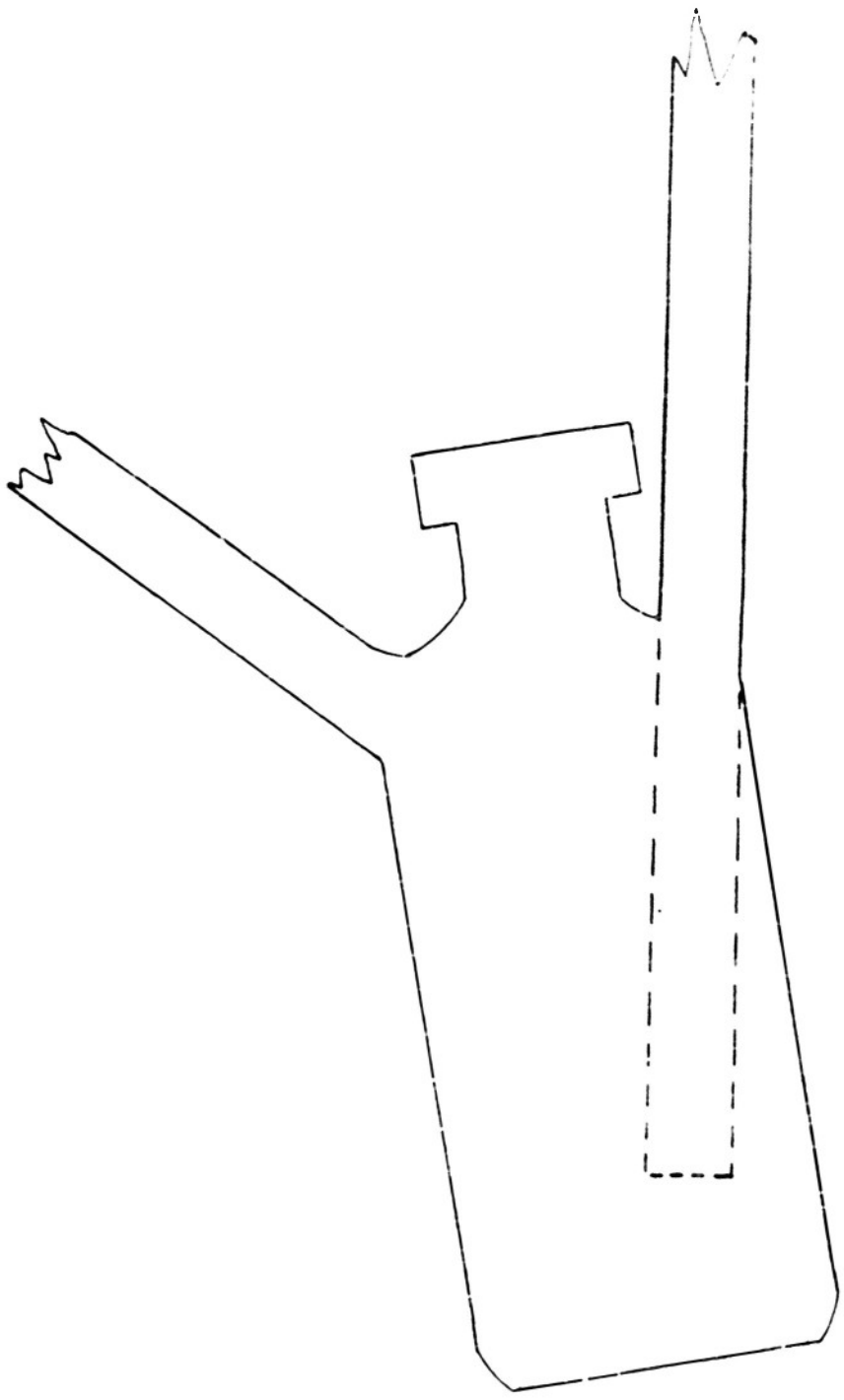
It may be that some of the metal fluorides formed by electrolysis in these cells were so soluble that they did not form as solids on the electrodes. This could have led to error, but not to the erratic behavior of the potentials of the cells. One who continues this work might do well to use metals whose fluorides have very low solubilities.

IV. SOLUBILITIES

General Experimental

The object of this work was to determine the solubilities of several fluorides of metals in hydrogen fluoride and to learn how the solubilities are correlated with the positions of the metals in the periodic system.

Polythene containers (see Plate II) were used to hold the solutions. These were constructed from eight ounce polythene bottles and half inch polythene tubing. Joints were welded with polythene strips. These bottles withstood attack by hydrogen fluoride quite well. When a new eight ounce bottle weighing 33 grams was filled with the solvent and allowed to stand for four days, it showed a gain of 16 milligrams in weight and a slight darkening in color. A second filling with hydrogen fluoride showed a weight equal to the second within one milligram. This is as close an agreement as one could hope for. Before new bottles were used for solubility work they were filled with hydrogen fluoride and allowed to stand for several days. The liquid was then removed before the bottles were used. When ten gram samples of hydrogen fluoride which had stood in a pre-treated bottle for a week were evaporated to dryness in platinum crucibles the amount of residue found in each case was less than 0.1 milligram. The bottoms of the crucibles seemed to lose some of their brightness, suggesting that a very thin residual film had been left



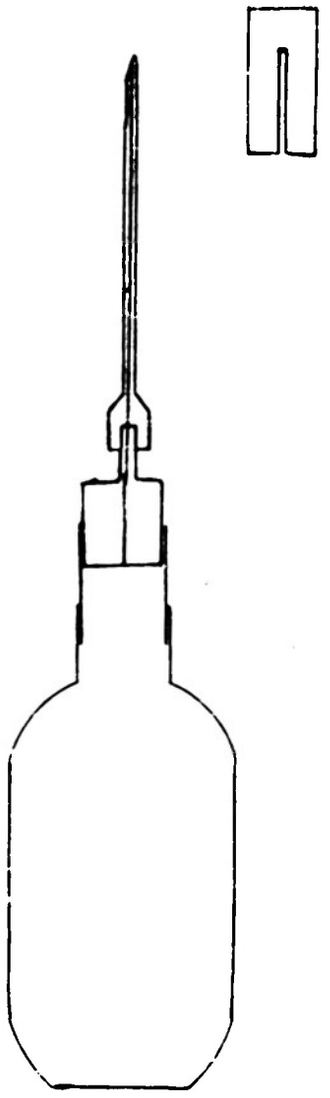
SAMPLE BOTTLE

PLATE II

behind. The specific conductance of hydrogen fluoride (7.6×10^{-4} chm^{-1} cm^{-1}) did not change on standing in a polythene conductivity cell for a day.

The solutions were made up by placing an excess of the fluoride concerned in solubility bottles and then distilling in hydrogen fluoride prepared in the manner described in the previous section. Fluorine, diluted with nitrogen usually was passed through the solution to convert any non-fluoride impurities in the salt to fluoride and to decompose any water present. This step was omitted when there was danger of oxidizing the salt. The bottles were closed with Teflon plugs in the tubes and were placed in a shaker in an air thermostat. Samples were withdrawn, usually at daily intervals. When no change in concentration was found over a three day period, the solutions were considered to be saturated. During this period the samples were mechanically shaken and a large excess of the solid was always present. Solubilities were measured at three different temperatures for each salt. In most cases the first determination was made at the highest temperature and the last at the lowest.

Samples were withdrawn from the bottles with the apparatus, shown in Plate III, made from a two ounce polythene bottle with a short piece of polythene tubing forced into the neck. An adapter to fit inside this tubing and to fit a number 20 hypodermic needle was machined from Teflon. When samples were to be withdrawn the sampler was allowed to come to the temperature of the solubility bottle. Air was expelled from the sampler by squeezing. The solubility bottle was then punctured with the needle; and the hand pressure released from the sampler. Solution flowed into the sampler. The sampler was quickly removed and capped with a piece of



SAMPLER

PLATE III

polythene which had a hole in it of nearly the same diameter as the needle. This made an effective seal which lasted long enough to enable one to weigh the sampler without losing sample. The puncture hole was sealed over with polytrifluorochloroethylene grease and was then covered with a film of polythene.

The usual method of determining the amount of solution present was to weigh the sampler and the contents by placing it in a saddle suspended from the beam of an analytical balance mounted over the top of a fume hood. The solution sample was then discharged into a weighed platinum crucible with cover and the empty sampler was weighed again. The solvent was evaporated by an infra red (heat) lamp in a hood. The crucible and contents were then dried to constant weight in an oven at 110°C. In several cases it was necessary to convert the remaining solid into a form more suitable for weighing. In some other cases the dried solid was analyzed to make certain it was the correct compound. In a few cases analyses of the solute were made without first driving off the hydrogen fluoride.

When a solubility determination was completed the cap was removed from the bottle and some of the solid in equilibrium with the solution at the lowest temperature was taken out of the bottle with a bent nickel spatula. This slurry was put into a brass centrifuge filter tube which had a filter screen made of 80 mesh copper gauze and was subjected to centrifugation to obtain a sample of the solid phase. This sample was then usually weighed in a platinum crucible and subsequently heated in an oven at 110°C to remove hydrogen fluoride. From the loss in weight the proportion of hydrogen fluoride of crystallization was calculated. It must be kept in mind that two obvious sources of error

occur here: (1) some liquid solution may have remained on the solid after centrifuging, (2) some hydrogen fluoride of crystallization may have been lost before the sample was weighed. Therefore, these analyses, while indicative of the composition of the solid, are not to be taken as the final proof of the existence of the compounds corresponding to the analyses.

The fluorides were obtained from several sources. Many of them were made by the action of liquid hydrogen fluoride upon the hydroxide, oxide, or carbonate of the metal. In nearly every case of this sort the fluoride formed was not very soluble. Hydrogen fluoride was added to the compound and allowed to react. Liquid hydrogen fluoride was then poured off, and more hydrogen fluoride was added. After several decantations of this sort the product was dried at 110°C. Zinc, cadmium, copper II, magnesium, cobalt II, nickel II, and lead II fluorides were made in this way from the carbonate. Bismuth trifluoride was made from the hydroxide while mercury I fluoride was made from the oxide.

Solutions of lithium fluoride were made from Baker's C. P. Analyzed lithium fluoride. Another solution was also made by reacting metallic lithium with hydrogen fluoride. These solutions gave the same solubility values.

The sodium fluoride used was Baker's C. P. Analyzed. The samples obtained by evaporation of the solvent were ignited at red heat to insure decomposition of any acid fluorides.

Beryllium fluoride was made by the action of hydrogen fluoride on Eimer and Amend C. P. beryllium nitrate with several additions and decantations of hydrogen fluoride.

Solutions of calcium fluoride were made by the action of hydrogen

fluoride upon the metal, and by dissolving calcium fluoride made by the action of hydrogen fluoride on precipitated calcium carbonate. The solutions gave values for the solubility which agreed well.

C. P. strontium fluoride was purified by allowing it to stand under anhydrous fluoride and pouring off the solution. This was done three times. After weighing some of the desolvated samples they were converted to the sulfate. The weight change was that to be expected from strontium fluoride.

Bausch and Lomb C. P. barium fluoride was treated in the same way as the strontium fluoride.

The mercury I fluoride solutions were analyzed by converting the solute to the chloride and weighing as such.

The Pennsylvania Salt Manufacturing Company generously furnished samples of several fluorides. Mercury II fluoride was one of them. They reported a fluorine analysis on the substance indicating 15.4% fluorine (theory 15.9%). The solute obtained by evaporating the solvent from solutions was analyzed by adding nitric acid, drying, adding water, drying, converting it to the oxide and weighing as such. The proportion of hydrogen fluoride in the solid phase was determined by pumping off volatile material under vacuum and determining the weight loss.

Aluminum fluoride was made by reacting aluminum dust with aqueous hydrofluoric acid. This gave a product which was subsequently heated to redness. The solid was then brought in contact with several portions of hydrogen fluoride which were poured off. This was done to insure complete dehydration.

Thallium I fluoride was prepared by dissolving Eimer and Amend metallic thallium sticks wound with a platinum wire catalyst in aqueous

hydrofluoric acid which attacked the metal very slowly. The water was evaporated away, the platinum was removed, hydrogen fluoride was added and later evaporated away. The high solubility of the solute made it impossible to pour off the liquid without losing most of the product. An analysis of this product showed 8.48% fluorine (theory 8.51%). When the solutions were analyzed for thallium I fluoride the weighed samples were added to an ice-water mixture, potassium iodide was added and the thallous iodide was filtered and dried and weighed as such.

Thallium III fluoride was made by passing fluorine diluted with nitrogen through a solution of thallous fluoride in hydrogen fluoride. The action of fluorine formed thallic fluoride which precipitated. Much of the fluorine passed through the solution without reaction. The supernatant solution over the precipitated thallic fluoride was poured off to remove the unreacted thallous fluoride. The solid thallic fluoride was washed twice by decantation with hydrogen fluoride. Finally it was mixed with hydrogen fluoride and was again treated with dilute fluorine. Weights of samples of the solid left after the evaporation of the solution agreed fairly well with the amount of thallic fluoride determined by the following analysis. The solute left behind after evaporation of a sample amounted to 1.1 milligram per gram of hydrogen fluoride while the analysis described below gave .81 milligram per gram of hydrogen fluoride. The first of these values is probably accurate to within only 20%. The solutions were analyzed by discharging weighed samples into concentrated potassium iodide solution. There was a large quantity of ice floating in the solution to absorb the heat of solution of hydrogen fluoride. The iodine set free was titrated with sodium thiosulfate solution using starch as indicator.

Silver I fluoride was made by reacting hydrogen fluoride with the carbonate and with the oxide. Since the product was quite soluble it was not practical to pour off the liquid. The solvent was evaporated, more hydrogen fluoride was added and evaporated several times. An analysis of this product showed 15.2% fluorine (theory 15.0%). The solutions and the solid were analyzed by converting the fluoride to the chloride and weighing as such.

Silver II fluoride was made and analyzed in the same manner as the thallic fluoride except that the solid was analyzed by converting it to argentous chloride and weighing as such. A sample of sclution when evaporated gave 2.9 milligrams of solid per gram of hydrogen fluoride, while titration of the solution gave 2.4 milligrams per gram of solution. The weighing was probably accurate within ±25%.

If a significant amount of the lower fluoride were present in the silver II and thallium III fluoride solution the amount of solid weighed after evaporation of the solvent would be much more than that determined iodimetrically. If a significant amount of fluorine were present in the solutions the amount determined iodimetrically would be higher than that determined gravimetrically. Since the values determined by both methods are in substantial agreement, there cannot be very much of either fluorine or lower fluoride present. Since the values reported are those determined iodimetrically, a small amount of fluorine in solution would add to the apparent stability.

Cerium III fluoride was made by dissolving G. Frederick Smith cerous nitrate (hydrated) in water and precipitating it with aqueous hydrofluoric acid. The liquid was filtered off. This product was dehydrated by adding several portions of hydrogen fluoride and pouring

off the supernatant liquid each time.

Cerium IV fluoride was furnished by the Pennsylvania Salt Manufacturing Company. They reported that an analysis gave 35.5% fluorine (theory 35.2%).

Zirconium tetrafluoride was made by the action of hydrogen fluoride upon the nitrate, followed by successive additions and decantations of hydrogen fluoride.

Thorium fluoride was made from hydrogen fluoride and Baker's C. P. thorium nitrate. Several portions of the liquid were added and decanted successively.

Antimony trifluoride was purchased from the Harshaw Chemical Company. It was treated with several portions of hydrogen fluoride before being used.

Manganese trifluoride was furnished by the Pennsylvania Salt Manufacturing Company. They reported an analysis indicating a fluorine content 50.2% (theory 50.9%). The solid obtained after evaporating hydrogen fluoride from the sample was analyzed by precipitating manganese dioxide with ammonium hydroxide and hydrogen peroxide and weighing as such. This analysis was checked by discharging a sample of solution into a concentrated potassium iodide solution mixed with ice, and titrating the iodine set free. A sample handled in this way indicated 36.2 milligrams of manganese trifluoride present while a gravimetric sample of the same size indicated 39.5 milligrams of manganese trifluoride present. This difference may be explained as being the consequence of volatilization of iodine due to the heat of reaction. The iodine volatilized to a large enough extent to give color to the vapor above the solution and some must have been lost. The solid in equilibrium

with the solution was analyzed by determining the weight loss when the volatile matter was evaporated under vacuum.

White iron II fluoride was prepared by the action of hydrogen fluoride upon the chloride. The procedure of several additions and decantations was used. No precipitate occurred when silver nitrate was added to an aqueous solution of the product. The sample of solute obtained by evaporating solutions showed no green color, indicating that no iron had been converted to the +3 state (which is green) in the handling.

Iron III fluoride was purchased from City Chemical Company, New York. It was highly hydrated. It was dehydrated by adding several portions of hydrogen fluoride and pouring them off. Conversion of samples of the resulting salt to the oxide by adding sulfuric acid and igniting indicated that it was anhydrous ferric fluoride. Since the solid obtained by evaporating solvent from samples of the solution had a tendency to hydrate during handling, it was analyzed by treating the dried samples with sulfuric acid and igniting to give ferric oxide. The weight loss was 29.3% (theory 29.2%).

Cobalt trifluoride was another substance furnished by the Pennsylvania Salt Manufacturing Company. Their fluorine analysis showed 48.5% fluorine (theory 49.2%). An analysis for fluorine on the solid left after evaporation of the solvent from a solution indicated 44.7% fluorine. Care had to be taken in handling this as moist air would attack the solid. When this happened it could easily be detected by a pronounced color change.

Results

The solubilities are expressed in Table II in grams of solute per 100 grams of solvent. The temperatures are in degrees centigrade. The values for the composition of the solid phase in equilibrium with the solution are given in terms of moles of hydrogen fluoride per mole of the metal fluoride.

The limits of error are reflections either of the precision obtained in the analyses or of the limits with which measurements could be made in the determinations. The larger of the limits obtained from these two considerations is the one recorded.

The solubility of the red product obtained by reacting cuprous oxide with hydrogen fluoride followed by decantation of the liquid and several subsequent additions and decantations of the liquid, was measured. It was hoped that this product would be copper I fluoride. X-ray powder patterns of a sample of the product show the presence of metallic copper. This suggests that disproportionation to copper II fluoride and copper may have occurred. The solubilities recorded were 0.073 $\pm$.003 @ 11.8°C, 0.074 $\pm$.002 @ -4.5°C, and 0.078 $\pm$.002 @ -22.5°C. These values are in terms of grams of solute per 100 grams of solvent. The solid analysis indicated 0.22 moles of hydrogen fluoride present per weight of solid corresponding to one mole of copper I fluoride. This tenfold increase in solubility over the solubility of copper II fluoride indicates that some compound other than copper II fluoride must have been present. Perhaps it was copper I fluoride.

Solubilities of commercial samples of chromium trifluoride and iron III fluoride were measured. Subsequent analysis showed these materials to be hydrated. The solubility of the ferric fluoride was

TABLE 2

SOLUBILITIES OF FLUORIDES IN HYDROGEN FLUORIDE

Salt	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Equilibrium Solid Phase Moles HF/ Mole Salt
LiF	12.2	10.33 ±.15	-3.3	10.31 ±.08	-23.0	10.30 ±.09	1.09
NaF	11.0	30.1 ±.2	-9.8	25.1 ±.1	-24.3	22.1 ±.1	4.10
BeF_2	11.2	0.015 ±.004	-5.1	0.013 ±.003	-24.2	0.014 ±.002	0.033
MgF_2	12.2	0.025 ±.003	-3.3	0.025 ±.004	-23.0	0.033 ±.002	0.25
CaF_2	12.2	0.817 ±.015	-3.3	1.061 ±.005	-23.0	1.444 ±.004	1.86
SrF_2	12.2	14.83 ±.09	-3.3	14.63 ±.004	-23.0	14.43 ±.002	3.22
BaF_2	12.2	5.60 ±.12	-3.3	4.74 ±.04	-23.0	3.612 ±.006	5.95
ZnF_2	14.2	0.024 ±.002	-4.4	0.019 ±.002	-23.0	0.016 ±.002	0.047
CdF_2	14.2	0.201 ±.009	-4.4	0.198 ±.001	-23.2	0.189 ±.001	0.068
HgF_2	11.9	0.544 ±.010	-7.8	0.623 ±.010	-25.2	0.609 ±.010	0.013
HgF	11.8	0.877 ±.005	-4.5	0.811 ±.020	-22.5	0.789 ±.019	0.00
CuF_2	12.4	0.01 ±.005	-8.3	0.008 ±.004	-23.1	0.01 ±.004	0.28
AgF	11.9	83.2 ±.8	-9.8	43.77 ±.03	-25.0	27.2 ±.7	1.94

TABLE 2 (Cont.)

Salt	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Equilibrium Solid Phase Moles HF/ Mole Salt
AgF_2	11.5	0.048 ±.006	-8.9	0.030 ±.002	-25.2	0.024 ±.001	0.0
TlF	11.9	580. ±45.	-7.8	450. ±50.	-25.2	305. ±15.	1.92
TlF_3	11.5	0.081 ±.003	-8.9	0.029 ±.005	-25.2	0.027 ±.003	1.04
AlF_3[a]	11.2	⩽0.002	-5.1	⩽0.003	-24.2	⩽0.004	0.22
CeF_3[b]	11.9	⩽0.043	-7.8	⩽0.037	-25.2	⩽0.041	0.53
CeF_4	11.9	0.10 ±.01	-9.8	0.10 ±.01	-23.8	0.106 ±.006	0.03
ZrF_4	12.4	0.009 ±.002	-8.3	0.015 ±.003	-23.1	0.023 ±.002	1.00
ThF_4[a]	11.8	⩽0.006	-4.5	⩽0.002	-22.5	⩽0.0007	0.840
PbF_2	12.4	2.62 ±.09	-8.3	3.56 ±.04	-23.1	3.67 ±.01	2.23
SbF_3	11.9	0.536 ±.005	-9.8	0.285 ±.010	-23.8	0.191 ±.003	0.13
BiF_3	12.4	0.01 ±.002	-8.3	0.01 ±.003	-23.1	0.01 ±.002	0.16
MnF_3	11.5	0.164 ±.004	-7.8	0.147 ±.010	-25.2	0.134 ±.003	0.11
FeF_2	11.8	0.006 ±.002	-4.5	0.005 ±.002	-22.5	0.005 ±.002	0.32
FeF_3	11.9	0.008 ±.002	-7.8	0.003 ±.002	-25.2	⩽0.001	0.60

TABLE 2 (Cont.)

Salt	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Temp. °C	Solubility g per 100 g of HF	Equilibrium Solid Phase Moles HF/ Mole Salt
CoF_2	14.2	0.036 ±.002	-4.4	0.033 ±.002	-23.2	0.040 ±.003	0.38
CoF_3	11.9	0.257 ±.003	-9.8	0.264 ±.015	-23.8	0.272 ±.016	0.35
NiF_2	11.9	0.037 ±.002	-9.7	0.040 ±.002	-25.0	0.035 ±.002	0.25

a. These solubilities were on the edge of the lower limit of solubility which could be observed by the method used.

b. A small amount of black material of undetermined composition was observed along with the dried samples and was weighed with them. The results are probably not much too high.

over a tenth of a gram per hundred grams of solvent, while that of the hydrated chromium trifluoride was over eight grams per hundred grams of solvent.

DISCUSSION

In Table III the various fluorides are listed along with the qualitative solubilities gathered by Simons (1), principally from the work of Fredenhagen (27), Klatt (28), Gore (29), and Franklin (30). He lists S as soluble, SS as slightly soluble (less than 1%), and I as insoluble. Many of the compounds are more soluble than would be anticipated from the qualitative data. While the value reported for the solubility of argentous fluoride agrees reasonably well with the literature value of 33 grams per 100 grams of solution at -15°C (27), the solubility of lithium fluoride is much higher than either of the literature values of 2.7 grams per 100 grams of solvent at 18°C (27) or 5.8 grams per 100 grams of solvent at 20°C (25).

In the same table the interpolated solubilities of the indicated fluorides in hydrogen fluoride in terms of grams of solute per 100 grams of solvent at 10°C are given. The solubility of the corresponding hydroxides or oxides are given for comparison. These values are for 25°C except where a temperature is indicated. They have been taken from Seidell (31) and have been recalculated in terms of grams per 100 grams of water. The ratio of solubility of fluorides in hydrogen fluoride at 10°C to solubility of the corresponding hydroxide in water at 25°C is also given.

In most cases there is a qualitative correlation between the

TABLE 3

SOLUBILITIES OF FLUORIDES IN HYDROGEN FLUORIDE VS

SOLUBILITIES OF HYDROXIDES IN WATER

Salt	Former Solubility	Solubility of Fluoride at 10°C grams/100 grams Solvent	Solubility of Hydroxide or Oxide at 25°C grams/100 grams Solvent	Ratio	Solid Phase Moles HF/ Mole Salt
LiF	S	10.33	12.9	0.78	1.09
NaF	S	29.9	114.	0.26	4.10
KF	S	36. (5)	117.	0.31	4. (5)
RbF	S	100 extrapolated (6)	174.	0.58	
CsF	S	213. (7)	308.	0.69	3. (7)
BeF_2	SS	0.015	(@ 20°C) 0.00001	2. x 10^3	0.033
MgF_2	SS	0.025	0.0027	9.2	0.25
CaF_2	SS	0.856	0.12	7.1	1.86
SrF_2	SS	14.81	0.87	17.	3.22
BaF_2	SS	5.48	4.68	1.2	5.95
ZnF_2	I	0.023	(@ 18°C) 0.0003	77.	0.067
CdF_2	I	0.200	0.0026	77.	0.068
HgF_2	I	0.551	0.0519	11.	0.013
HgF	-	0.871	9 x 10-11	1. x 10^{10}	0.00
CuF_2	I	0.01	.0003	30.	0.28
AgF	S	79.2	.0022	36. x 10^3	1.94
AgF_2	-	0.076			0.0
TlF	S	560.	62.	9.0	1.92
TlF_3	-	0.047	--		1.04
AlF_3	I	0.002	(@ 18°C) 0.001	2.	0.22
CeF_3	I	0.043			0.53
CeF_4	-	0.10			0.03
ZrF_4	-	0.01			1.00

TABLE 3 (Cont.)

Salt	Former Solubility	Solubility of Fluoride at 10°C grams/100 grams Solvent	Solubility of Hydroxide or Oxide at 25°C grams/100 grams Solvent	Ratio	Solid Phase Moles HF/ Mole Salt
ThF_4		0.006			0.840
PbF_2	I	[illegible]	(@ 20°C) 0.0012	23.00	2.23
SbF_3	-	3.535			0.13
BiF_3	I	0.09	(@ 20°C) 0.0014	7.	0.16
InF_3	I	0.360			0.11
FeF_2	I	0.006	3.8×10^{-4}	16.	0.32
FeF_3	I	0.008	$4. \times 10^{-9}$	$2. \times 10^{6}$	0.60
CoF_2	I	0.036			0.38
CoF_3	-	0.259			0.35
NiF_2	-	0.037	.0013	29.	0.25

solubility of fluorides in hydrogen fluoride and hydroxides in water. However the large differences in the solubility ratios indicate that some of the factors influencing the solubilities of fluorides in hydrogen fluoride are different from those influencing the solubilities of hydroxides in water.

Fredenhagen and Cadenbach (27, 32, 33) have given evidence to show that when many normally acidic substances dissolve in hydrogen fluoride, they act as bases according to the equation

$$MA + 2HF = M^{+} + H_2A^{+} + 2F^{-}$$

The boiling point elevations and conductivities observed when these compounds are dissolved in the solvent argue for this type of reaction. This indicates that the solvent is extremely acidic. One might then expect that fluorides would be stronger bases in hydrogen fluoride than would the corresponding hydroxides in water. This would help to explain why many of the fluorides are more soluble in hydrogen fluoride than are the corresponding hydroxides in water.

It is interesting to note an increase in solubility with increasing atomic number in the first main group of the periodic table.

In the second main group the trend is preserved except that either strontium fluoride or barium fluoride is out of place. The solid phase analysis indicates that the solid phase in equilibrium with strontium fluoride solution probably is a trihydrofluoride, while the barium fluoride solid phase appears to be a hexahydrofluoride. The previously studied (5, 6, 7) binary phase systems involving hydrogen fluoride have shown that when a change in solid phase composition occurs there is a decrease in solubility as the solid becomes more solvated. It is likely

that if a trisolvated barium fluoride existed at the temperatures involved, it would be more soluble than is strontium fluoride trihydrofluoride.

The second subgroup shows a well behaved increase in solubility with increasing atomic number.

The solubilities of lithium, beryllium, and aluminum fluorides decrease in that order.

As would be anticipated, the fluorides of mercury, silver, and thallium show greater solubility in the lower oxidation state than in the upper since lower oxidation states are more basic. The lower fluorides of silver and thallium are even more soluble than would be anticipated. While their counterparts in the water system are strong bases there may be a factor other than basicity which causes the high solubility of these fluorides in hydrogen fluoride or water.

Iron, cobalt, and nickel difluorides show an increasing solubility in that order. Cobalt and nickel difluorides show nearly the same solubilities.

The fluorides of iron, cobalt, and cerium all show a higher solubility in the higher oxidation state than in the lower. This is hard to explain. The fact that antimony trifluoride is so much more soluble than bismuth trifluoride is also puzzling. The solubilities of plumbous and manganic fluorides also are larger than one would predict from the solubilities of the hydroxides.

Calcium fluoride, mercuric fluoride, lead difluoride, zirconium tetrafluoride, and cobalt trifluoride all show decreasing solubilities with increasing temperature.

The large solubility of the hydrated ferric fluoride relative to

the anhydrous salt leads one to speculate that an aquo ion is formed or that the fluoride is amphoteric and dissolves because water acts as a strong base. The latter property of water should cause this substance, when present as an impurity, to have a large influence upon the solubilities of most fluorides. Water would introduce extra fluoride ions ($H_2O + HF = H_3O^+ + F^-$) which would influence solubilities through the common ion effect or through the dissolving of amphoteric fluorides. Since FeF_6^{-3} forms in aqueous solution it is unlikely that $Fe(H_2O)_n^{+3}$ would form in hydrogen fluoride containing much fluoride ion. On this account, the effect of water upon the solubility of ferric fluoride indicates that the latter probably is amphoteric.

In Table III the number of moles of hydrogen fluoride per mole of salt found in the solid phase is listed. Numbers less than 0.25 indicate that the salt is probably unsolvated. Where the values are close to integers, it is likely that the solid phase composition corresponds to that indicated by the integer. The significance of numbers far from integers is not clear. It appears that many fluorides crystallize with hydrogen fluoride of solvation.

In the first main group of the periodic table it has been shown that the degree of solvation increases with increasing atomic number. The compound LiF·HF which is indicated in these studies has been reported by Berzelius (36).

In the second main group the solid phase indicated goes from unsolvated beryllium fluoride to a hexasolvated strontium fluoride paralleling the effect in group I.

In subgroup II all of the fluorides are unsolvated.

Argentous and thallous fluorides both must give a solid phase

with two moles of hydrogen fluoride per mole of salt. $AgF \cdot 3HF$ (34) and $AgF \cdot HF$ (35) have both been described previously. Argentic fluoride is unsolvated while thallic fluoride seems to be associated with one mole of solvent.

Since thorium and zirconium (and hafnium) tetrafluorides are isomorphous, it is interesting to note that a monohydrofluoride is indicated for both of them.

Lead difluoride seems to have a solvated solid phase, probably a dihydrofluoride.

It might be desirable to investigate the compositions of some of the solid phases further in order to establish the significance of the fractional ratios of moles of solvent to salt. Conductivity measurements should give more accurate values for the solubilities of the less soluble fluorides.

SUMMARY

The solubilities of the fluorides of metals in hydrogen fluoride in general qualitatively parallel the solubilities of the corresponding hydroxides in water and are in the order which one would predict from the periodic table. There are, however, several unexplained exceptions.

Many fluorides of metals form solid solvates with hydrogen fluoride. The degree of solvation of the solid phase by hydrogen fluoride seems quite consistent when comparing similar compounds.

Zinc and copper fluorides are essentially not amphoteric in hydrogen fluoride. However, the high solubility of a hydrated ferric fluoride suggests that water acting as a base increases the solubility of ferric fluoride.

Ethyl chloride and normal pentane give no indications of forming solid clathrate compounds with hydrogen fluoride. Methylene chloride and chlorine also appear not to form such compounds; however more work is needed to settle this point.

Many electrodes in liquid hydrogen fluoride have irreproducible potentials. No reversible electrodes were found. Voltage-current curves indicate high overvoltages associated with electrode processes.

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